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APPLICATION

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TITLE: FIBER REINFORCED COMPOSITE AND METHODS OF FORMING THE SAME

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FIBER REINFORCED COMPOSITE AND METHODS OF FORMING THE SAME

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority from U.S. provisional patent application Serial No. 60/436, 466, which is entitled "Fiber Reinforced Composite Product with Flexible Longitudinal Geometry," filed December 27, 2002, and is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to fiber reinforced composites and methods of forming such composites.

BACKGROUND OF THE INVENTION

[0003] Fiber reinforced composites (FRC) are useful, for example, as substitutes for metal materials. A fiber reinforced plastic wire can have strength comparable to a steel wire but only a fraction of the weight thereof. Fiber reinforced plastic wires can also be made more aesthetically pleasing to the eyes than steel wires do. They are therefore good replacements of metal wires used, for instance, in orthodontic treatments.

[0004] FRC wires can be produced by pultrusion. In a typical pultrusion process, a continuous reinforcement is first impregnated with curable resin and then pulled through a rigid die having a tunnel with a desired cross-section. The resulting long wire has a fiber inner core and a composite cover layer. The composite is cured in the die so that the wire can retain its cross-sectional shape. When cured, a soft material is hardened as chemical bonds are formed between atoms and/or molecules, which may occur for example under radiation. For example, monomers may be cured to produce polymers. After curing in the die,

the resulting wire will retain a cross-section similar in size and shape to that of the die tunnel.

[0005] If desirable, the wire is subject to further processing such as longitudinal shaping and further curing. Post-pultrusion processing is commonly referred to as "beta-staging." Under known approaches, to shape a wire longitudinally, the composite is only partially cured in the die, separated from the die, longitudinally shaped, and then fully cured.

[0006] An example FRC pultrusion process is described in U.S. Patent No. 5,869,178, issued on 9 February 1999 to Kusy *et al.* ("Kusy"), the content of which is incorporated herein by reference.

[0007] However, the known approaches to producing pultruded FRC have certain drawbacks. For example, under these known approaches, fiber distribution in the resulting composite wire is often uneven when the fiber content is in a certain percentage range. The manufacturing process can be complicated as two curing steps are required if the composite wire is to be shaped longitudinally. It is also difficult to produce very thin wires as it is difficult to insert resins into a very small opening of the die. Further, pulling a fiber through a very thin tunnel may induce high stress in the fiber. A highly stressed fiber is easy to break, either during or after the pultrusion process.

[0008] Thus, there is a need for improved fiber reinforced composites and improved methods of forming fiber reinforced composites.

SUMMARY OF THE INVENTION

[0009] There is provided a process for forming a fiber reinforced composite in which a shrinkable die is used, so that a composite of fiber and resin placed in the die can be compressed by shrinking the die to form a desired transverse cross-section.

[0010] In accordance with an aspect of the present invention, there is provided a method of forming a fiber reinforced composite. The method includes placing a composite of fiber and resin in an elongate tunnel of a shrinkable die; shrinking the die to reduce the transversal cross-section of the tunnel along a longitudinal extent of the tunnel so as to compress the composite of fiber and resin in the tunnel; and curing the composite of fiber and resin.

[0011] There is also provided a process for forming a fiber reinforced composite in which a flexible die is used so that the die can be bent to shape the composite.

[0012] The method is particularly well suited to form wire for use in orthodontic treatment.

[0013] Other aspects, features and advantages of the invention will become apparent to those of ordinary skill in the art upon review of the following description of specific embodiments of the invention in conjunction with the accompanying figures.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] In the figures, which illustrate exemplary embodiments of the invention,

[0015] **FIG. 1** is a flowchart illustrating a process of forming a fiber reinforced composite;

[0016] **FIGS. 2** to **4** schematically illustrate a process incorporating the processes of **FIG. 1**;

[0017] **FIG. 5** is a cross-sectional view of a fiber reinforced plastic wire produced by the process illustrated in **FIGS. 2** to **4**; and

[0018] **FIG. 6** is a graph comparing the properties of a composite wire with a metal wire.

DETAILED DESCRIPTION

[0019] A flow diagram of an exemplary process **S100** for forming a fiber reinforced composite is illustrated in **FIG. 1**. In process **S100**, a composite of fiber and resin is placed in an elongate tunnel of a shrinkable die (**S102**); the die is shrunk to reduce the transversal cross-section of the tunnel of the die along a longitudinal extent of the tunnel so as to compress the composite in the tunnel (**S104**); and the composite is then cured (**S108**). The composite may be fully or partially cured in the die so that it may retain its shape after it is separated from the die. The die may be shrunk sufficiently to compress the composite into a pre-determined transversal cross-sectional shape.

[0020] Optionally, the die may be bent lengthwise so as to shape the composite in the die (**S106**), prior to curing (**S108**). Optionally, the die could be bent lengthwise before shrinking (**S104**). Since both shrinking and bending can be performed before curing the composite, only one curing step is required.

[0021] After curing, the die is peeled from the composite in step **S110**.

As can be appreciated by a person skilled in the art, in process **S100**, the tunnel of the die does not have to have a small transversal cross-section initially, even when the desired cross-section of the composite wire is small. The composite of fiber and resin can therefore be placed in the die with an initially large tunnel cross-section. Since the composite is compressed into the desired cross-sectional shape under mainly radial pressures, the stress in the resulting product is small. Further, since the tunnel of the shrunk die can have a size substantially smaller than its pre-shrunk size, it is easier to insert resins into the die initially even if the transversal cross-section of the final product is small.

[0023] **FIGS. 2** to **4** schematically illustrate an exemplary physical embodiment of process **S100** for producing a fiber reinforced composite wire having a desired size and shape.

[0024] As illustrated in **FIG. 2** a section of composite fiber **12** impregnated

with uncured resins is placed into an elongate tunnel (not shown) of a shrinkable and flexible die **14** (**S102**). Impregnated fiber **12** includes a bundle of fiber strands (yarns) and resins impregnated thereon. The fibers may be impregnated with the resins in suitable manners known to persons skilled in the art, such as those used in conventional pultrusion processes.

[0025] For unidirectional composites, each of the fiber strands has a length longer than the length of the tunnel of die **14**. The bundle of fiber strands may be impregnated before or after it is placed into the tunnel of die **14**. For other composites, fibers may be shorter than the tunnel of die **14**.

[0026] Impregnated fiber **12** can include one strand or filament or a bundle of strands or filaments of fiber materials. Suitable fiber materials include metals, ceramics, glasses, polymers, and the like. For example, suitable fiber materials include boron, aluminium, quartz, graphite, polyethylene, nylon, and any combination thereof. Commercially available fiber yarns or rovings may be used. The fiber yarns or rovings may be preformed using known textile manufacturing techniques, such as brading. The fibers may contain one or more other ingredients, such as coupling agents, primer agents, and sizing agents, for improving the properties of the product or for facilitating the manufacturing process, such as improving the bonding between the resin and the fibers. Fibers can be chosen depending on the intended purpose for the final product. For example, for producing aesthetic composite product such as orthodontic wire, glass fiber may be preferable.

[0027] The resins used may include any suitable resins used in conventional pultrusion processes. Monomer resins may be used. Exemplary suitable monomer materials include acrylic monomer, acrylate monomer, epoxy monomer, carbonate monomer, or any combination thereof. The resins may contain a suitable polymerization initiator. For producing orthodontic wires, Bis-GMA based dental resins, such as Metafil FLo™ supplied by Sun Medical, may be used. These resins have been commonly used in dentistry and are

biocompatible in an oral environment. Further, they can form products with an aesthetically pleasing appearance.

[0028] The tunnel of die **14** is longitudinally straight and has a uniform cross section. The tunnel of die **14** for receiving fiber and resin may have any desired shape suitable for producing the desired final product. This allows formation of a wire having a cross-section that can be virtually any shape depending on the application. In the depicted embodiment, the cross-section is circular.

[0029] The initial cross-section of the die tunnel can have a size substantially larger than the desired size of the cross-section of the resulting composite wire.

[0030] Die **14** is oriented so that the tunnel is vertically disposed. However, the tunnel may be otherwise disposed. The vertical orientation is advantageous because the gravitational force is normal to the transversal cross-section of the tunnel and does not contribute to the transverse force exerted on the strands in the tunnel.

[0031] Preferably die **14** is made of material that may contract in size (or shrink) so as to constrict the tunnel formed therein. As well, die may be formed of a material that may be bent or flexed along its length. The shrinkable and/or flexible materials suitable for formation of die **14** are known to persons skilled in the art and are readily available. For example, the die may be formed with temperature sensitive material that shrinks in response to heat. One suitable material for such a die is polyolefin. An example of a suitable die material is the heat-shrinkable tubes available under the tradename SUMITUBE™. Other suitable polymers include polytetrafluoroethylene (PTFE), perfluoroalkoxy (PFA), fluorinated ethylene polymer (FEP), polyvinydene Fluoride (PVDF), and polyethylene terephthalate (PET).

[0032] Fiber **12** may be pulled into and through the tunnel of die **14**, such as is done in conventional pultrusion processes. Fiber **12** may then be cut into a desired length. A portion of fiber **12** is exposed at each end of die **14**. Each

exposed portion can be, for example, two inches long. Two weights **16A** and **16B** may be respectively tied to one or other of the two exposed end portions. The weights **16A** and **16B** pull the fiber strands so that fiber **12** is straightened.

[0033] Optionally additional resin can be injected into die **14** with an injecting device such as syringe **18** to further fill the die tunnel.

[0034] Die **14** is then shrunk by heat treatment using heat gun **20** so as to cause the tunnel to contract and die **14** to compress fiber **12** and resin therein into a desirable cross-sectional shape (**S104**), as illustrated in **FIG. 4**.

[0035] It may be advantageous to shrink die **14** gradually from top to bottom along the length of the tunnel of die **14** as gravity facilitate the removal of excessive resin. The temperature required to shrink die **14** may vary depending on the die material. A heat gun producing hot air with a temperature of about 180°C has been found suitable for shrinking a polyolefin die. Die **14** preferably shrinks uniformly so that the cross section of its tunnel retains its general shape, but decreases in size. The contracting tunnel exerts a force on the uncured composite therein, thereby compressing the composite and causing it to assume a cross-section shape that is the shape of the tunnel.

[0036] Optionally, impregnated fiber **12** and die **14** can be placed under vacuum together after a section of die **14** has been shrunk to remove any gas entrapped inside the tunnel before completely shrinking die **14**. For example, the top 10% of die **14** may be shrunk first before vacuuming and further heating.

[0037] As illustrated in **FIG. 4**, after die **14** is completely shrunk to the desired size a section **22** can be cut out from the die and the impregnated fiber assembly (**S104**). Section **22**, including die **14** can then be bent along its length into a desired profile **24** (**S106**), for example, with an arch-shaped mould. Profile **24** can then be cured in a curing chamber **26** (**S108**). Profile **24** can be cured in manners known to a person skilled in the art, such as by radiation. For example, profile **24** may be cured with UV-light for about 90 seconds. After profile **24** is cured, die **14**

is separated from the fiber reinforced composite. A small cut/slit may be made at one end of die **14** and it may be peeled from the cured composite and discarded

[0038] The resulting fiber reinforced composite wire may be used in a variety of applications. For example, it may be used in orthodontic treatments.

[0039] The cross-section of a fiber reinforced composite wire produced as described above is shown in **FIG. 6**. The example wire has a glass fiber content of 48% by volume. As can be seen, glass fibers are evenly distributed. As is known to a person skilled in the art, in wires produced by conventional pultrusion processes, fiber distribution is often uneven when the fiber content is in a certain range, as shown in figures 6a to 6f of Kusy and discussed therein.

[0040] The resulting composite may contain a matrix and reinforcement. The reinforcement is formed of the fiber, while the cured resins form a polymer matrix. The resulting polymer may be a homopolymer, copolymer, terpolymer, and blends or modifications thereof. Copolymers include block, graft, random and alternating copolymers. The polymers may have various structures, such as isotactic, syndiotactic and random molecular configurations, which can be either linear or cross-linked.

[0041] Depending on the input fiber and resin, the resulting polymer product can be wholly or partially absorbable, non-absorbable, dissolvable, or biodegradable.

[0042] Test results show that fiber reinforced composite orthodontic wires produced with process **S100** can meet the specifications of international standards such as the ASTM D 790 standard. The fiber reinforced composite orthodontic wires have similar or improved mechanical properties in comparison with conventional metal orthodontic wires such as Ni-Ti wires sold under the tradename Reflex™ by TP Orthodontics, Inc. As shown in **FIG. 6**, a composite wire can withstand higher load than a similarly sized Ni-Ti wire having 0.45 mm (0.018 inch) diameter. The composite wire was formed of a Bis-GMA matrix

based dental resin, Metafil Flo B12, from Sun Medical reinforced with a bundle of several E-glass fiber yarns, each containing 200 fiber filaments (the filament diameter = 9μm, Unitica Glass Fiber Co. Ltd, Japan. The fiber volume fraction was 48% and the diameter of the wire was 0.5mm. As can be seen, the composite wire also showed good recovery upon unloading.

[0043] Advantageously, with a shrinkable die, the die tunnel can have a large initial cross-section. As a result, it is easy to insert the fiber and resin into the tunnel and the stress in the fiber resulting from insertion of the composite and removal of the wire can be reduced. Very thin composite wires can thus be formed. Further, multiple strands of fiber can be evenly distributed in the formed composite, thus improving the mechanical properties of the composite. When a flexible die is used, the die can be bent to shape the composite wire before the wire is separated from the die. Only one curing step is required to form an arched wire.

[0044] Modifications to the exemplary embodiment described above are possible, as will be understood and appreciated by persons skilled in the art.

[0045] For example, die **14** can be horizontally arranged instead of vertically. Die **14**, with fiber and resin in it, may be shrunk first then shaped longitudinally or shaped longitudinally first then shrunk. Die **14** can also be shrunk in other manners. Heat gun **20** may be replaced by other heating devices, such as those using electromagnetic radiations. The whole assembly of impregnated fiber **12** and die **14** may be placed in a heating chamber.

[0046] The fiber content may vary depending on the desired mechanical properties, as will be understood by persons skilled in the art. Generally, increasing fiber content can increase the mechanical strength and stiffness of the final wire. Braided fibers may be used as the reinforcement fiber. Similarly, Short fibers or particulate reinforcement can also be used and inserted into die **14**. Pigments may be added to the resin before shrinking die **14**, to, for example, give the final product a desired colour.

[0047] Although only exemplary embodiments of this invention have been described above, those skilled in the art will readily appreciate that many modifications are possible. The invention, rather, is intended to encompass all such modification within its scope, as defined by the claims.